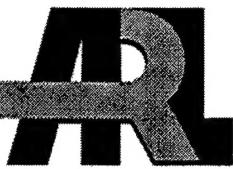


ARMY RESEARCH LABORATORY



Development of Water-Reducible Polyurethane Coating for Military Applications

by John A. Escarsega, Dawn M. Crawford,
Jeffrey L. Duncan, and Kestutis G. Chesonis

ARL-TR-1950

May 1999

19990628 039

Approved for public release; distribution is unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

ARL-TR-1950

May 1999

Development of Water-Reducible Polyurethane Coating for Military Applications

John A. Escarcega, Dawn M. Crawford, Jeffrey L. Duncan, and
Kestutis G. Chesonis
Weapons and Materials Research Directorate, ARL

Abstract

The U.S. Army Research Laboratory's Coatings Research Team has developed a water-reducible (WR) chemical agent resistant coating (CARC) utilizing hydroxy-functional polyurethane dispersions and water-dispersible polyisocyanates. This coating has met the Army requirement for chemical agent resistance, while having a volatile organic compound (VOC) content of less than 220 g/l, and it provides improved weather durability, flexibility, and mar resistance. It has undergone field application testing at Letterkenny Army Depot and at Fort Sill. A military specification is being developed, and U.S. Patent #5,691,410 has been awarded.

Since CARC is used on a wide variety of Department of Defense (DOD) equipment, users include painting installations across DOD (such as Army Depots, Marine Corps Logistics Bases, and Air Force Logistics Centers) and original equipment manufacturers. Application of the WR CARC at these sites can reduce VOC emissions by millions of pounds per year and, combined with the improved performance properties, will potentially avert costly expenditures for pollution abatement equipment while sustaining all Army mission requirements.

Acknowledgments

The authors would like to acknowledge the following individuals for their technical input and assistance toward this effort: Mr. Kurt Best (Bayer Corporation) and Messrs. Bhaskar Urs and Mike Reschel (Hentzen Coatings).

INTENTIONALLY LEFT BLANK

Table of Contents

	<u>Page</u>
Acknowledgments.....	iii
List of Figures	vii
List of Tables	vii
1. Introduction	1
2. Background.....	2
3. Experimental.....	3
3.1 Sample Preparation	3
3.2 Panel Tests.....	4
3.3 Thermal Analysis	4
4. Results and Discussion.....	6
4.1 Coating Properties	6
4.2 Thermal Analysis	8
5. Conclusions	14
6. References	17
Distribution List	19
Report Documentation Page.....	21

INTENTIONALLY LEFT BLANK

List of Figures

<u>Figure</u>		<u>Page</u>
1.	DSC Heating Scan of SOL After 10-Day Dry Time	9
2.	DSC Cooling Scan of SOL After 10-Day Dry Time.....	9
3.	DSC Heating Scan of WR 3.5 After 10-Day Dry Time	10
4.	DSC Cooling Scan of WR 3.5 After 10-Day Dry Time.....	10
5.	Storage Module vs. Temperature at 1.1 Hz After 6-Month Dry Time.....	12
6.	Tan δ vs. Temperature at 1.1 Hz After 6-Month Dry Time	12
7.	Loss Modulus vs. Temperature at 110 Hz After 17-Day Dry Time	14

List of Tables

<u>Table</u>		<u>Page</u>
1.	General Test Requirements	5
2.	DS2 Resistance and Hardness Evaluation.....	5
3.	Impact Resistance and Flexibility	7
4.	Tan δ and Tg at 1.1 Hz	14

INTENTIONALLY LEFT BLANK

1. Introduction

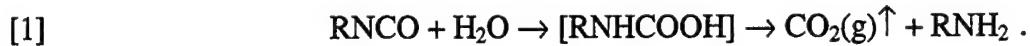
One of the most demanding challenges that has faced the coating industry in recent years has been the effort to reduce volatile organic compounds (VOC). This effort has also been a major focus for the U.S. Army Research Laboratory's Coatings Research Team. Currently there is a tremendous need for camouflage coatings that will satisfy diverse Army mission requirements and provide reduced VOCs. The basic camouflage topcoat required on all Army tactical vehicles and aircraft is a very low gloss (at 60° <1.0 and at 85° <3.5) two-component, solvent-based polyurethane. This high solid, solvent-based topcoat has a maximum VOC content of 420 g/l. This coating provides the standard characteristics, such as corrosion resistance and durability, of any automotive protective finish. It is also required to provide resistance to chemical warfare agents, be resistant to chemical agent decontamination procedures, and provide camouflage properties in the visible and near-infrared regions to minimize detection.

To meet current and anticipated Environmental Protection Agency (EPA) regulations as well as military requirements, the U.S. Army Research Laboratory's Coatings Research Team has developed a water-reducible, two-component polyurethane coating, implementing water-dispersible hydroxyl-functional polyurethane and water-dispersible polyisocyanates. This material has a VOC of 180 g/l, a greater than two-fold improvement over the currently used solvent-based system. Additionally, this new water-reducible system maintains chemical agent resistance (CAR) and exhibits superior physical properties, such as low temperature flexibility, impact resistance, and weathering durability, compared to the current solvent-based system.

The work described herein details the research and development of the water-reducible coating and the U.S. Army requirements for chemical agent resistant coatings (CARC). Thermal characterization utilizing differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) of the most recent formulations as well as traditional coating test results are presented. DMA is discussed and compared to coating properties such as impact resistance.

2. Background

Historically, it has been critical to ensure that water is not present in nonaqueous, two-component polyurethane formulations due to its undesirable reaction with isocyanate. The reaction between water and isocyanate forms an unstable carbamic acid. The carbamic acid quickly decomposes to generate carbon dioxide and amine (reaction [1]); the amine then reacts with additional isocyanate to yield a substituted urea (reaction [2]) (Woods 1990; Oertel 1985).



In a solvent-borne, two-component system, this reaction may inhibit or adversely affect the stoichiometry and development of cross-linking that is crucial to the integrity and performance typical of two-component polyurethane coatings. However, recent developments in water-borne polyurethane technology have enabled high-performance coatings to be formulated using water-dispersible polyisocyanates and hydroxyl-functional polyurethane dispersions (Jacobs and Yu 1993). While there is a competing reaction occurring with water, the kinetics, raw materials, and proper indexing of isocyanate (NCO) to hydroxyl (OH) groups used in the formulations ensure that sufficient cross-link density is established in the film. In two-component water-reducible polyurethane coatings, the water-dispersible aliphatic polyisocyanate reacts slowly with water. Thus, an excess of polyisocyanate will preferentially react with the hydroxyl groups of the polyurethane dispersion. Jacobs and Yu (1993) proposed that because the polyisocyanate is dispersed and not dissolved in water, it coalesces with the polyol dispersion particles, enabling the isocyanate group to be close enough to the hydroxyl group for cross-linking to occur. More recent work by Hegedus et al. details a mechanism of film formation for two-component waterborne polyurethane systems in terms of a time line of integrated events (Hegedus, Gilicinski, and Haney 1996; Bassner and Hegedus 1996). Their work indicates that the dispersion of isocyanate in an aqueous system appears

to occur immediately upon addition and mixing. The authors found that particle coalescence during the admixed state was minimal using particle size experimentation.

Traditionally, solvent-based systems are formulated with a slight excess of NCO (NCO:OH approximately equal to 1.1:1.0). This excess NCO ensures complete reaction of the polyol and provides optimal film properties. In water-borne formulations, higher amounts of NCO are required to account for the competing reaction between isocyanate and water. Typically, water-borne formulations are indexed using excess NCO ranging from 1.5 to 3.5. Early efforts within our laboratory focused on formulations with NCO to OH ratios of 2.0:1.0 and 3.5:1.0. While these films exhibited enhanced properties compared to the solvent-based coating, they did not have the necessary chemical resistance to pass the Army's live agent requirement. For this reason, further investigation led to the most recent formulations with NCO to OH ratios of 5.0:1.0. This level of indexing provided chemical agent resistance without a significant change in coating properties.

3. Experimental

3.1 Sample Preparation. The coatings were sprayed onto cold rolled steel panels pretreated with zinc phosphate (Bondrite 37) and a chromate sealer (Parcoolene 60) unless otherwise noted. The panels were sprayed to a dry film thickness of 45–55 μm . Formulations reported in this paper were pigmented, conforming to color number 34094, green 383, as stated in MIL-C-46168D, the U.S. Army specification for two-component polyurethane coatings. Throughout this report, water-reducible formulations are designated “WR,” followed by the specific NCO indexing. The solvent-based system is designated as “SOL.” The water-reducible formulations implement water-dispersible hydroxy-functional polyurethane and water-dispersible polyisocyanates with conventional siliceous-type extenders for flattening purposes, as well as prime pigments used to make the base green camouflage coating.

DMA and DSC were performed on free coating films. These films were prepared by spraying the coating onto release paper. The films were dried for 10 days at ambient temperature before

separating them from the release paper. The handling and testing of free films require greater thickness than coated panel testing. The solvent-based coatings had an average film thickness of 280 μm , and the water-reducible free film thickness measured approximately 160 μm . Although these film thicknesses were different, the data were normalized according to individual sample dimensions and therefore could be qualitatively compared.

3.2 Panel Tests. Table 1 lists the general coating tests that are specified in MIL-C-46168. The procedures for each test are detailed in the military specification. Chemical agent resistance was determined by subjecting the coated panel to the liquid agent, bis-dichloroethyl sulfide (mustard gas), and allowing the sample to sit for 30 min. The surface of the panel was then rinsed with isopropanol. The residual agent vapor was collected using bubblers after 4 hr and again after an additional 18 hr following the isopropanol rinse. The residual vapor after each interval was reported in micrograms.

Table 2 summarizes the color difference and pencil hardness evaluations that were used to determine the decontamination solution no. 2 (DS2) resistance of the films. DS2 is an alkaline-based material used for field decontamination after chemical agent exposure. Its basic formulation consists of diethylenetriamine (70%), sodium hydroxide (2%), and ethylene glycol monomethyl ether (28%). DS2 resistance requires color stability and film integrity. Films used for these tests were drawn down on 76-mm \times 152-mm tin-plated panels. The dry film thickness was measured to be 45–55 μm . The coated panels were air dried for 7 days at ambient temperature. The test procedure involved applying 1.5 mm of DS2 to a 1-in-diameter circular area on the panel surface and allowing the DS2 to sit for 30 min undisturbed. Afterwards, the panel was thoroughly rinsed with water. The pencil hardness tests were performed in accordance with ASTM D3363 (6.01) on exposed and unexposed areas on the panel.

3.3 Thermal Analysis. DSC was performed using a TA Instruments 2920 DSC. The experimental method involved cooling the film from ambient to -65°C , followed by heating at $10^\circ\text{C}/\text{min}$ to $+200^\circ\text{C}$. The temperature was then held isothermally at 200°C for 2 min and recooled to -65°C . Data were collected during both the heating and cooling cycles. The experiment was conducted under a nitrogen purge of approximately $50\text{ cm}^3/\text{min}$.

Table 1. General Test Requirements

Test	Color	VOC (g/l)	Specular Gloss	Water Resistance	Hydrocarbon Resistance	Chemical Agent Resistance (μ g)
Mil-C-46168D	$E_{NBS} \leq 2.0^a$	≤ 420	$60^\circ \leq 1.0$ $85^\circ \leq 3.5$	168-hr Immersion	168-hr Immersion	≤ 180
WR 3.5	$E_{NBS} \approx 1.41$	≈ 180	$60^\circ \approx 0.9$ $85^\circ \approx 1.7$	No Blisters	No Blisters	510
WR 5.0	$E_{NBS} \approx 1.69^a$	≈ 180	$60^\circ \approx 0.9$ $85^\circ \approx 2.2$	No Blisters	No Blisters	98

^a Hunter's Revised National Bureau of Standards (NBS) color difference equation.

Table 2. DS2 Resistance and Hardness Evaluation

Material	NBS Color Difference After DS2 Exposure ^a (Requirement ≤ 2.0)	Pencil Hardness Unexposed/Exposed
WR 3.5	1.36	HB/HB
WR 5.0	0.43	2H/2H
SOL	0.57	HB/HB
3.5 Index (Clear Coat)	5.03	H/F
4.0 Index (Clear Coat)	6.56	B/B
4.5 Index (Clear Coat)	1.54	HB/HB
5.0 Index (Clear Coat)	0.67	HB/B
5.5 Index (Clear Coat)	9.84	HB/3B

^a Hunter's Revised National Bureau of Standards (NBS) color difference equation.

DMA of the coating films was performed using an Imass Inc. Autovibron (automated Rheo-200 Rheovibron, Toyo Instruments). This instrument is a forced oscillation dynamic mechanical analyzer that places the film in oscillating tension at very small strain rates, allowing evaluation of the material in the linear viscoelastic range. The samples were evaluated over a temperature range between -100° C and $+150^\circ \text{ C}$ at a heating rate of $2^\circ \text{ C}/\text{min}$. Data were collected at 1.1 Hz and 110 Hz to observe the effect of frequency on dynamic mechanical behavior.

4. Results and Discussion

4.1 Coating Properties. General panel test results of WR 3.5 and WR 5.0 are shown in Table 1. The second column of the table lists the MIL-C-46168 requirement for each test. With the exception of chemical agent resistance, both water-reducible formulations fell well within the specified requirements. The specification requires no more than 180 µg of residual agent vapor after 22 hr of sampling. It should be noted that WR 5.0 provided exceptional chemical agent resistance (98 µg). Although WR 3.5 exhibited similar properties to WR 5.0, it does not meet the requirement for chemical agent resistance (510 µg). Both WR 3.5 and WR 5.0 demonstrated excellent hydrocarbon (an 85% isoctane/15% toluene blend) and water resistance.

The coated panels were also evaluated for DS2 resistance. MIL-C-46168 requires that the panels retain color stability and hardness after exposure to DS2 in accordance with the procedure described in the Experimental section of this report. Pencil hardness was also measured prior to and following DS2 exposure. These results are listed in Table 2.

An acceptable color change in the coatings after DS2 exposure is \leq 2.0 color units. WR 3.5 and WR 5.0 demonstrated good color stability. Clear coats at various degrees of indexing were evaluated to determine the DS2 resistance of the resin system. These data show that a minimum of 3.5 indexing is required to achieve DS2 resistance. The DS2 results indicate acceptable resistance with indexing at 4.5. It should be noted that obtaining DS2 resistance does not guarantee live chemical agent resistance (i.e., WR 3.5). Indexing at 5.0 results in excellent DS2 resistance and chemical agent resistance; however, indexing at levels above 5.0 results in film incompatibility.

Pencil hardness was determined to ensure that excessive softening of the film did not occur after DS2 exposure. An acceptable change in hardness should be within two hardness units or no softer than level "B." All films tested met this requirement with the exception of the clear coat indexed at 5.5, which apparently did not have proper film formation.

Good impact resistance and flexibility of coatings are generally associated with enhanced durability and wear. The current solvent-based system exhibits marginal impact resistance and low temperature flexibility. The water-reducible formulations show dramatically improved properties as shown in Table 3. Flexibility tests were performed on tin-plated, thin-rolled steel panels. SAE 1010 cold-rolled steel panels (untreated) were used for impact testing. Panels for both tests were sprayed to a dry film thickness of 45–55 µm. The films were dried for 10, 17, and 24 days at ambient temperature prior to testing. Impact resistance and flexibility were tested according to ASTM D 2794 and ASTM D 522 method B, respectively.

Table 3. Impact Resistance and Flexibility

Sample	Elapsed Dry Time (days)	Forward Impact Resistance (in-lbs)	Flexibility	
			at 25° C	at 0° C
WR 3.5	10	160	Pass	Borderline Pass
	17	148	Pass	Pass
	24	148	Pass	Borderline Pass
WR 5.0	10	148	Pass	Pass
	17	84	Pass	Pass
	24	100	Pass	Borderline Pass
SOL	10	52	Pass	Fail
	17	48	Pass	Fail
	24	28	Pass	Fail

Wet and dry adhesion evaluations were conducted on initial water-reducible formulations (Escarcega and Duncan 1996). Numerous substrates and primers were utilized for the adhesion testing. These studies indicated that there was no incompatibility or adhesion problems with water-reducible formulations indexed up to 3.5. Current testing with WR 5.0 suggests similar adhesion properties. Extensive accelerated weathering studies utilizing a xenon light source were conducted on initial water-reducible formulations indexed at 3.5. These films exhibited a greater than two-fold improvement in weathering durability compared to the conventional solvent-based system. Water-reducible formulations indexed at 5.0 are currently being evaluated for accelerated weathering and outdoor exposure. Similar results to WR 3.5 are expected.

4.2 Thermal Analysis. DSC was performed on the conventional solvent-borne system and the water-reducible systems at both 3.5 and 5.0 indexing. Figures 1 and 2 show the DSC heating and cooling scans of the solvent system after the film was dried for 10 days. Over this temperature range, the sample exhibited two endothermic transitions: a small peak at about 33° C followed by a broad, much larger transition with a peak temperature of approximately 174° C. The glass transition temperature (T_g) was not evident in the DSC scans, which was most likely due to masking by the broad endothermic transitions. When the material was recooled (Figure 2), a clear T_g was observed at about 62° C. This T_g does not represent the actual T_g of the film because it was measured after the film was heated to 200° C. Exposure of the coating film to such temperatures most likely induced additional cross-linking, resulting in a higher T_g .

Figure 3 shows the DSC scan of WR 3.5 during the heating cycle. The thermal characteristics of the water-reducible film were distinctively different from the solvent system. The water-reducible system exhibited a sharp endotherm with a peak temperature of approximately 120° C. Another broad endothermic transition was also apparent at a lower temperature. It is not clear whether this broad transition is related to the T_g or another type of endothermic relaxation. When the sample was recooled, a sharp exothermic transition was observed with a peak temperature of 77° C, as shown in Figure 4. The magnitude of the exothermic transition was less than that of the melt observed during the heating cycle. It is believed that the sharp endotherm and exotherm observed in the water-reducible film is due to melting and recrystallization, respectively, of a polymeric additive present in the water-reducible formulations. The presence of this additive results in distinctively different thermal profiles of the water-reducible and solvent-borne systems. The thermal characteristics of the water-reducible films measured by DSC were independent of indexing ratios of 3.5 and 5.0.

DMA was used to investigate the effect of indexing and dry time on overall dynamic mechanical properties. T_g and modulus determinations were made on the water-reducible formulations and the conventional solvent-based system. Data were taken at both high (110 Hz) and low (1.1 Hz) frequency with the presumption that the higher frequency measurement may correlate better with mechanical properties such as impact resistance. The use of DMA to characterize coating films can

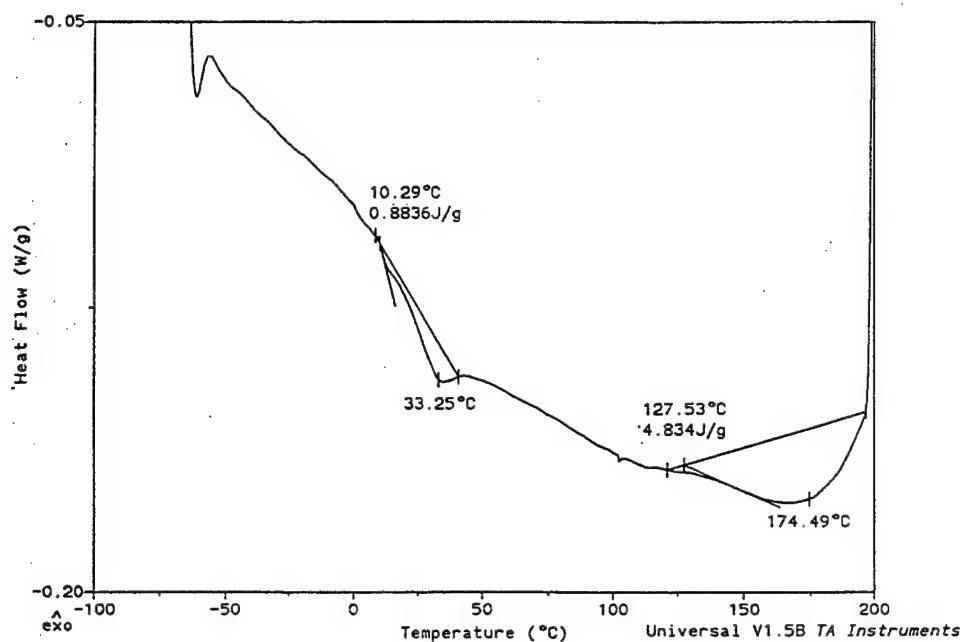


Figure 1. DSC Heating Scan of SOL After 10-Day Dry Time.

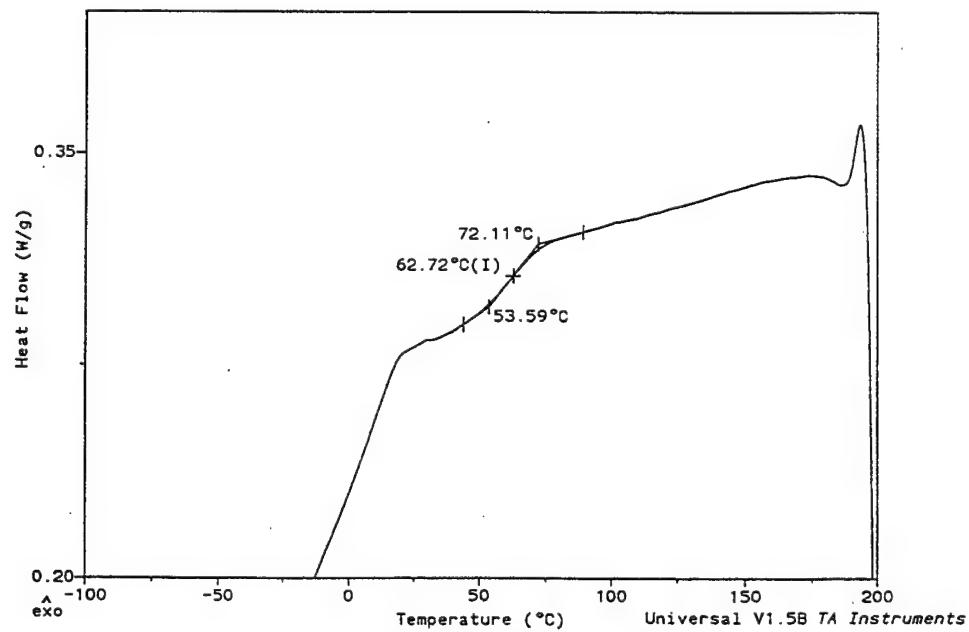


Figure 2. DSC Cooling Scan of SOL After 10-Day Dry Time.

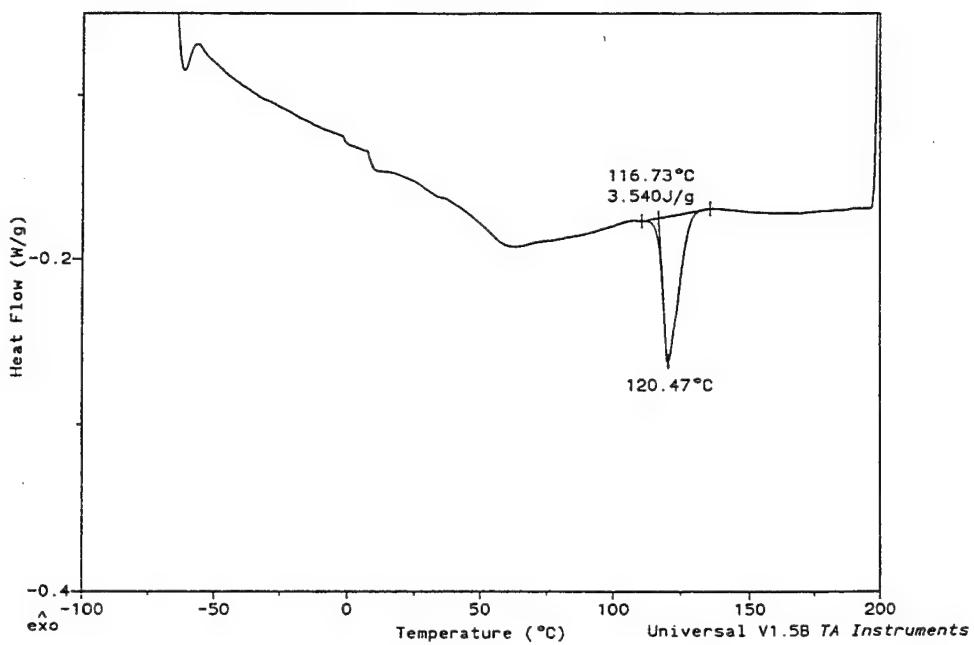


Figure 3. DSC Heating Scan of WR 3.5 After 10-Day Dry Time.

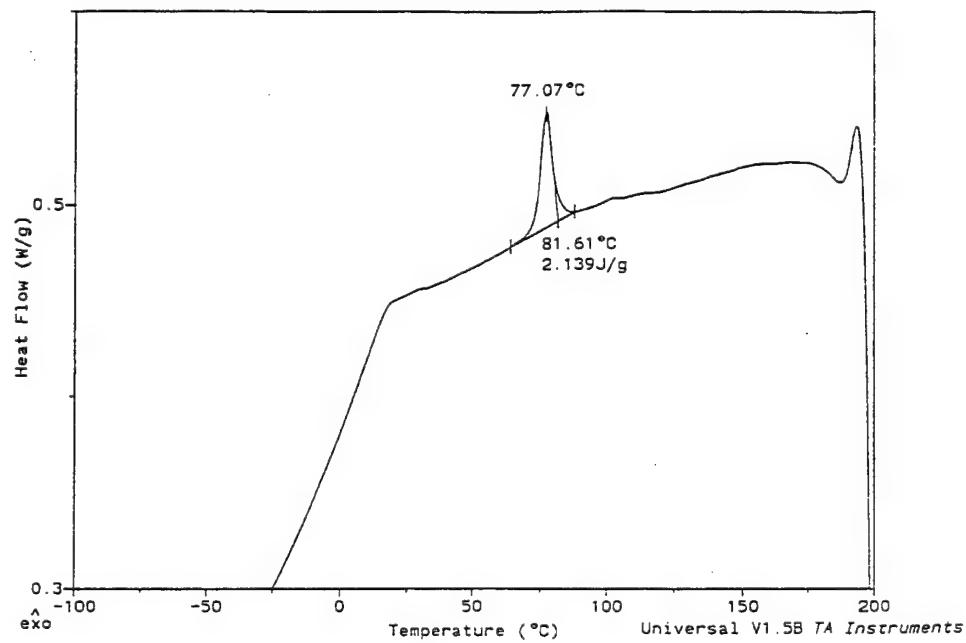


Figure 4. DSC Cooling Scan of WR 3.5 After 10-Day Dry Time.

provide valuable information regarding chemistry, morphology and performance properties. Detailed reviews of the application of DMA to study coatings can be found in the literature (Skrovanek and Schoff 1988; Hill 1992; Neag 1995; Wicks, Jones, and Pappas 1994).

Storage modulus (E') is a measure of a material's stiffness and can be used to provide information regarding polymer molecular weight, degree of cure and cross-link density (Skrovanek and Schoff 1988; Hill 1992; Neag 1995). Figure 5 shows the log (E') vs. temperature of WR 5.0 and SOL films after a dry time of approximately 6 months. The striking difference in the two films is seen primarily in the lower glass transition and higher storage modulus of the solvent-borne system. The upward rise in the modulus of the solvent system as the test progresses is indicative of temperature-induced cross-linking. The water-reducible system appears to exhibit a broader transition with lower E' in the rubbery plateau region and shows no signs of further cross-linking. The difference between the storage modulus ($\Delta E'$) in the plateau regions before and after the glass transition is generally related to the degree of cross-link density. A smaller $\Delta E'$ is related to greater cross-link density (Skrovanek and Schoff 1988; Hill 1992). The DMA data indicate that the solvent-based system exhibits greater cross-link density than the water-reducible systems.

Loss modulus (E'') and $\tan \delta (E''/E')$ are measures of a material's viscous response or the amount of energy dissipated as heat during deformation (Skrovanek and Schoff 1988; Hill 1992; Neag 1995). E' and $\tan \delta$ can provide information related to the polymer Tg and indicate damping properties of polymers. Figure 6 shows $\tan \delta (E''/E')$ vs. temperature of the same films shown in Figure 5. At the glass transition, $\tan \delta$ goes through a maximum. The temperature at which this maximum occurs is defined here as the Tg. These data clearly show the difference in the glass transition between the solvent and water-reducible systems. The solvent system exhibited a Tg of 37.6° C at 1.1 Hz, and the Tg of the water-reducible system was 91.6° C at the same frequency. This dramatic difference in Tg of the two systems is likely the reason for the improved properties of the water-reducible coating. Raw materials used in the water-reducible system result in a lower pigment volume concentration (PVC) than the solvent-borne system, eliminating excessive porosity and producing a more resin-rich film (Escarsega and Duncan 1996). This is not only important for achieving chemical agent resistance but may also reduce free volume in the polymer, leading to a

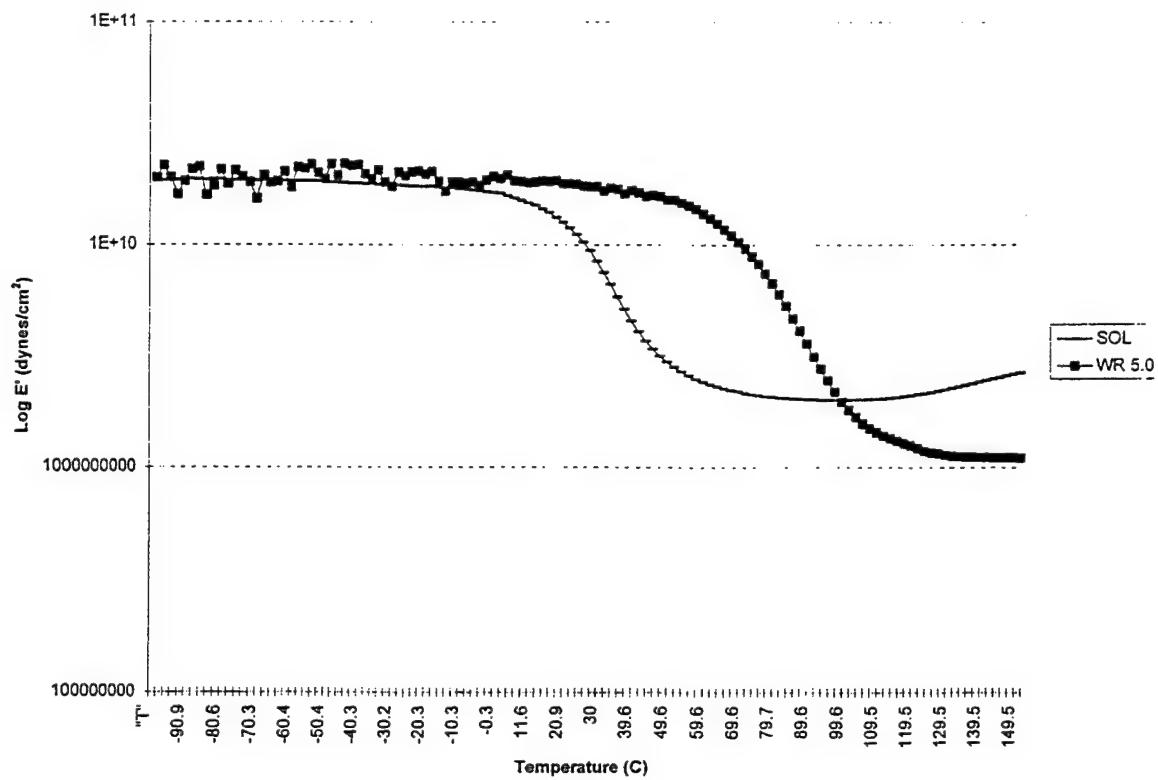


Figure 5. Storage Modulus vs. Temperature at 1.1 Hz After 6-Month Dry Time.

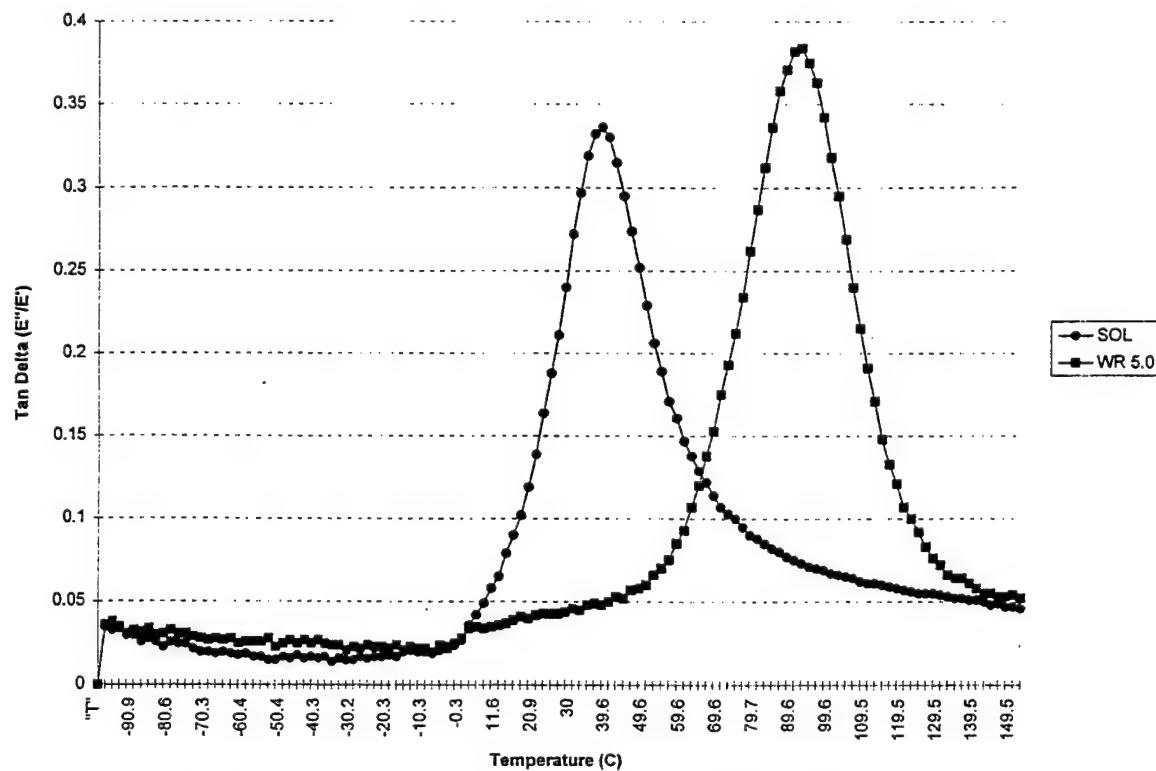


Figure 6. Tan δ vs. Temperature at 1.1 Hz After 6-Month Dry Time.

higher Tg. The flatter E' in the rubbery plateau region of the water-reducible films (Figure 5) suggests that these films exhibit a more complete cross-linking reaction than the solvent-based system and therefore are not susceptible to thermally induced cross-linking. This can be attributed to the negligible amount of "trapped" solvent present in the water-reducible systems.

The presence of low-temperature transitions on E'' or tan δ plots suggest enhanced flexibility and impact properties (Hill 1992; Neag 1995). E'' was determined at high frequency (110 Hz) to provide better correlation to the coating's impact resistance tests. Figure 7 shows the log E'' vs. temperature for the solvent system and the water-reducible systems indexed at 3.5 and 5.0. These data were taken after a 17-day dry time. The solvent-based system exhibits the classic β peak in the region of -50° C, which is used as a predictor of good impact resistance (Hill 1992). However, WR 5.0 and WR 3.5 exhibit broader loss modulus peaks, and WR 3.5 exhibits high loss modulus throughout the low-temperature region. This suggests greater molecular motion associated with the WR 3.5 film, which is in agreement with its superior impact resistance as shown in Table 3. Future work will involve impact testing at low-temperature, where greater differences in the films should be seen. The DMA data suggest that due to the high and broad E'' throughout the low-temperature region of this experiment, WR 3.5 is likely to exhibit superior low-temperature impact resistance.

The Rheovibron data indicate that the water-reducible film is more stable over time than the solvent-based system. Table 4 shows the Tg and the tan δ peak magnitude for WR 5.0 and the solvent system at intervals of drying between 10 days and 6 months. The solvent system initially exhibits a much higher tan δ than WR 5.0, but after 6 months of dry time this value drops below that of WR 5.0. Tan δ of WR 5.0 remains relatively stable throughout the drying period. This large change in tan δ peak magnitude of the solvent system may be due to solvent loss that occurs for the most part between 24 days and 6 months of drying and may translate to reduced properties of the solvent-based system over time. However, further studies would need to be conducted to confirm this possibility. WR 5.0 exhibits a significant increase in Tg between 24 days and 6 months of dry time. This increase in Tg of the water-reducible system could possibly result from densification or free-volume change that occurs as a result of aging (Hill 1992).

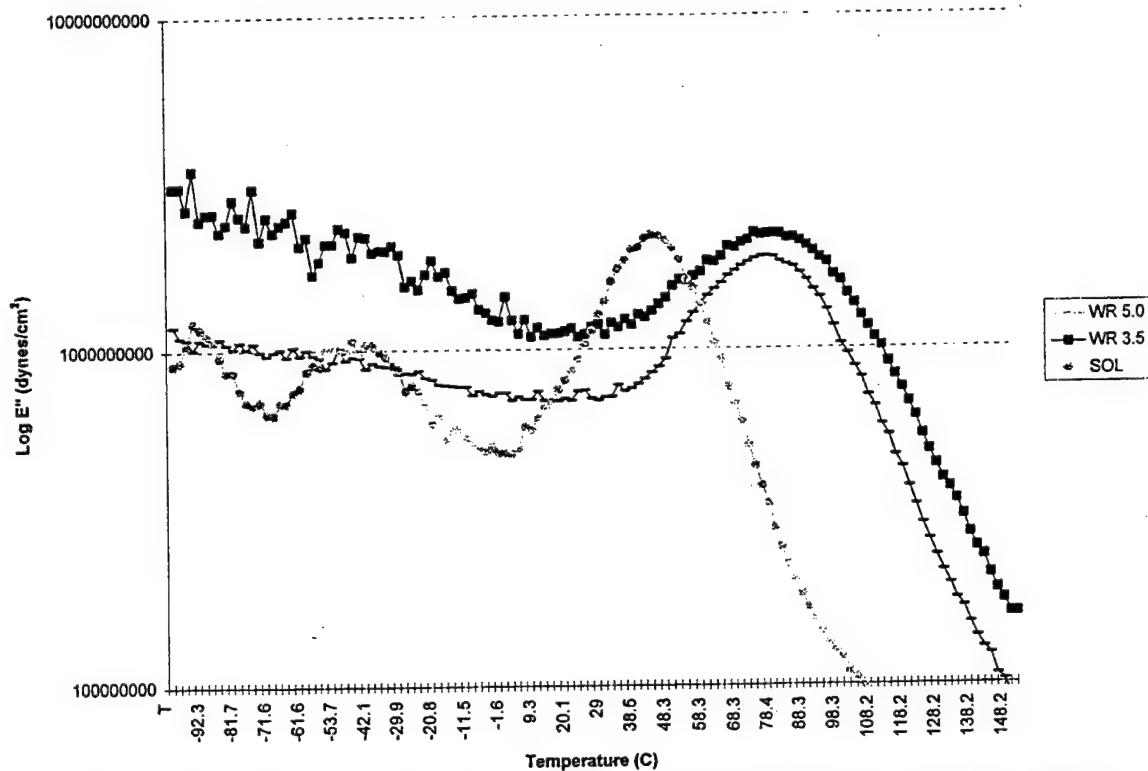


Figure 7. Loss Modulus vs. Temperature at 110 Hz After 17-Day Dry Time.

Table 4. Tan δ and Tg at 1.1 Hz

Material	Dry Time	Tg (°C)	Tan δ
SOL	10 days	43.6	0.584
	17 days	39.7	0.554
	24 days	37.7	0.557
	6 months	37.6	0.328
WR 5.0	10 days	73.6	0.379
	17 days	75.6	0.392
	24 days	79.6	0.388
	6 months	91.6	0.384

5. Conclusions

The U.S. Army Research Laboratory's Coatings Research Team has successfully formulated a low-VOC, water-reducible coating that is chemical agent resistant. The enhanced properties such as flexibility and durability have numerous implications for tri-Service implementation and usage.

It is anticipated that this material can be reformulated, incorporating minor pigmentation changes, to meet Air Force, Navy, and Marine Corps needs. Current efforts involve technology transfer from the laboratory to a production environment. Evaluation of large-scale application and durability of the coating on military vehicles is underway.

Thermal characterization of the coating films has provided insight into the chemical/morphological differences between the conventional solvent-based coating and the water-reducible formulations. Specifically, the dramatic increase in the Tg of the water-reducible coating and the breadth of the loss modulus transition seems to be related to the enhanced properties of the water-reducible films. The comparatively high values of loss modulus of WR 3.5 in the low-temperature region indicates that this material may exhibit superior impact resistance and flexibility at low temperatures. DMA data also indicated that the water-reducible films exhibit greater stability as a function of dry time compared to the solvent-based coating.

The formulations discussed in this report used conventional diatomaceous silica or siliceous-type extenders. To achieve low values for gloss ($60^\circ \leq 1.0$ and $85^\circ \leq 3.5$), other formulations are being developed using polymeric and/or nonsiliceous type materials. The higher efficiency of nonsiliceous materials as flattening agents allows lower quantities to be used compared to conventional diatomaceous silica, thus reducing the resin demand and enhancing mar resistance of the film. Unlike siliceous extenders that tend to dominate the surface of the current CARC system, the nonsiliceous material tends to integrate within the film matrix and interact with the resin system.

Future efforts will focus on establishing application parameters such as temperature, humidity, handling, and mixing procedures on both siliceous and nonsiliceous formulations. The coating tests and DMA data show that WR 3.5 has excellent film properties and actually exhibits better impact resistance than WR 5.0. For these reasons, future studies will involve re-evaluating of WR 3.5 for live chemical agent resistance and formulating new coatings at indexing levels between 3.5 and 5.0 in an effort to reduce costs associated with the isocyanate.

INTENTIONALLY LEFT BLANK.

6. References

- Bassner, S. L., and C. R. Hegedus. "A Review of Two-Component Water-Borne Polyurethane Coatings for Industrial Applications." *Journal of Protective Coatings and Linings*, vol. 13, no. 9, pp. 52–65, 1996.
- Escarzega, J. A., and J. L. Duncan. "A Water Reducible Environmentally Compliant Chemical Agent Resistant Coating." ARL-TR-1089, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, May 1996.
- Hegedus, C. R., A. G. Gilicinski, and R. J. Haney. "Film Formation Mechanism of Two-Component Waterborne Polyurethane Coatings." *Journal of Coating Technology*, vol. 68, no. 852, pp. 51–61, 1996.
- Hill, L. W. "Structure/Property Relationships of Thermoset Coatings." *Journal of Coating Technology*, vol. 64, no. 808, pp. 29–41, 1992.
- Jacobs, P. B., and P. C. Yu. "Two Component Waterborne Polyurethane Coatings." *Journal of Coating Technology*, vol. 65, no. 822, pp. 45–55, 1993.
- Neag, M. *Coatings Characterization by Thermal Analysis*. ASTM Manual 17, American Society for Testing and Materials, Philadelphia, PA, 1995.
- Oertel, G. *Polyurethanes Handbook*. New York: Hanser Publishing, 1985.
- Skrovanek, D. J., and C. K. Schoff. "Thermal Analysis of Organic Coatings." *Progress in Organic Coatings*, vol. 16, pp. 135–163, 1988.
- Wicks, Z. W., F. N. Jones, and S. P. Pappas. *Organic Coatings Science & Technology*. Vol. 2, New York, pp. 105–131, 1994.
- Woods, G. *The ICI Polyurethanes Book*. New York: John Wiley & Sons, 1990.

INTENTIONALLY LEFT BLANK

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
2	DEFENSE TECHNICAL INFORMATION CENTER DTIC DDA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218	1	DIRECTOR US ARMY RESEARCH LAB AMSRL DD J J ROCCHIO 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	HQDA DAMO FDQ D SCHMIDT 400 ARMY PENTAGON WASHINGTON DC 20310-0460	1	DIRECTOR US ARMY RESEARCH LAB AMSRL CS AS (RECORDS MGMT) 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	OSD OUSD(A&T)/ODDDR&E(R) R J TREW THE PENTAGON WASHINGTON DC 20301-7100	3	DIRECTOR US ARMY RESEARCH LAB AMSRL CI LL 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	DPTY CG FOR RDE HQ US ARMY MATERIEL CMD AMCRD MG CALDWELL 5001 EISENHOWER AVE ALEXANDRIA VA 22333-0001		<u>ABERDEEN PROVING GROUND</u>
1	INST FOR ADVNCED TCHNLGY THE UNIV OF TEXAS AT AUSTIN PO BOX 202797 AUSTIN TX 78720-2797	4	DIR USARL AMSRL CI LP (305)
1	DARPA B KASPAR 3701 N FAIRFAX DR ARLINGTON VA 22203-1714		
1	NAVAL SURFACE WARFARE CTR CODE B07 J PENNELLA 17320 DAHLGREN RD BLDG 1470 RM 1101 DAHLGREN VA 22448-5100		
1	US MILITARY ACADEMY MATH SCI CTR OF EXCELLENCE DEPT OF MATHEMATICAL SCI MAJ M D PHILLIPS THAYER HALL WEST POINT NY 10996-1786		

INTENTIONALLY LEFT BLANK.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</p>			
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	May 1999	Final, Aug 97 - Aug 98	
4. TITLE AND SUBTITLE Development of a Water-Reducible Polyurethane Coating for Military Applications		5. FUNDING NUMBERS 1L162618AH80	
6. AUTHOR(S) John A. Escarcega, Dawn M. Crawford, Jeffrey L. Duncan, and Kestutis G. Chesonis			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WM-MA Aberdeen Proving Ground, MD 21005-5069		8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-1950	
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The U.S. Army Research Laboratory's Coating Research Team has developed a water-reducible (WR) chemical agent resistant coating (CARC) utilizing hydroxy-functional polyurethane dispersions and water-dispersible polyisocyanates. This coating has met the Army requirement for chemical agent resistance, while having a volatile organic compound (VOC) content of less than 220 g/l, and it provides improved weather durability, flexibility, and mar resistance. It has undergone field application testing at Letterkenny Army Depot and at Fort Sill. A military specification is being developed, and U.S. Patent #5,691,410 has been awarded.			
Since CARC is used on a wide variety of Department of Defense (DOD) equipment, users include painting installations across DOD (such as Army Depots, Marine Corps Logistics Bases, and Air Force Logistics Centers) and original equipment manufacturers. Application of the WR CARC at these sites can reduce VOC emissions by millions of pounds per year and, combined with the improved performance properties, will potentially avert costly expenditures for pollution abatement equipment while sustaining all Army mission requirements.			
14. SUBJECT TERMS water-reducible polyurethane, DSC, DMA, VOC		15. NUMBER OF PAGES 23	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number/Author ARL-TR-1950 (Escarzega) Date of Report May 1999

2. Date Report Received _____

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

Organization

**CURRENT
ADDRESS**

Name _____

E-mail Name

Street or P.O. Box No.

City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

Organization

**OLD
ADDRESS**

Name _____

Street or P.O. Box No.

City, State, Zip Code

(Remove this sheet, fold as indicated, tape closed, and mail.)
(DO NOT STAPLE)